

Repulsion Between Finite Charged Plates with Strongly Overlapped Electric Double Layers

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Abstract

The screened Coulomb interaction between uniformly charged flat plates is considered at very small plate separations for which the Debye layers are strongly overlapped, in the limit of small electrical potentials. If the plates are of infinite length, the disjoining pressure between the plates decays as an inverse power of the plate separation. If the plates are of finite length, we show that screening Debye layer charges close to the edge of the plates are no longer constrained to stay between the plates, but instead spill out into the surrounding electrolyte. The resulting reduction in the disjoining pressure is calculated analytically. A similar reduction of disjoining pressure due to loss of lateral confinement of the Debye layer charges should occur whenever the sizes of the interacting charged objects become small enough to approach the Debye scale. We investigate the effect here in the context of a two dimensional model problem that is sufficiently simple to yield analytical results.

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The theory of the screened Coulomb DLVO repulsive force between colloidal particles with like charge, due to Derjaguin and Landau¹ and Verwey and Overbeek,² underpins our understanding of the stability of colloidal suspensions against flocculation and has subsequently been improved and extended.^{3–7} Careful measurements using atomically smooth mica surfaces,^{8,9} atomic force microscopes¹⁰ and laser optical tweezers^{11,12} have confirmed the theory within its expected range of validity. Increased interest in non-DLVO repulsive interactions acting at separations of only a few nanometers, a distance of the same order as that of the attractive dispersion forces,^{13,14} necessitates a careful analysis of DLVO forces at very small particle separations where the classical weak overlap approximation for the electric potential between the particles fails. Philipse *et al.* proposed an alternative approach¹⁵ in which the double layers are so strongly overlapped that the space between the two opposing surfaces is essentially at uniform potential. For surfaces of fixed charge, the resulting disjoining pressure was shown¹⁵ to diverge algebraically with the gap width. Here we revisit this regime of strongly overlapped Debye layers but suppose that the plates confining the electrolyte are of finite lateral extent. This may be regarded as the simplest instance of a broader class of problems where there is a loss of confinement of the Debye layer on a lateral scale that is comparable in magnitude to the Debye length. Examples include plate like clay particles,^{16–18} nanocolloids and the tips of AFMs.

We show that in this case some of the neutralizing charge between the opposing faces spills out of the gap at the edge of the plates, resulting in a reduction of the disjoining pressure. Such loss of confinement of the Debye layer charge has been previously investigated in cylindrical nanopores¹⁹ in the context of electroosmosis, and leads to a significant reduction of electroosmotic flux. It can be seen in numerical computations,¹⁸ but its effect upon the force between particles has not been investigated analytically.

We consider the simplest possible plane 2D model: a dielectric slab of thickness $2L$ split into two parts by a slot of width $2h \ll L$ occupying the region $-h < x < h$, as shown in Figure 1. The region outside the solid is occupied by an electrolyte (permittivity ϵ , Debye length $\kappa^{-1} \gg h$). There is fixed surface charge of density σ on each of the opposing faces $x = \pm h$, but the rest of the

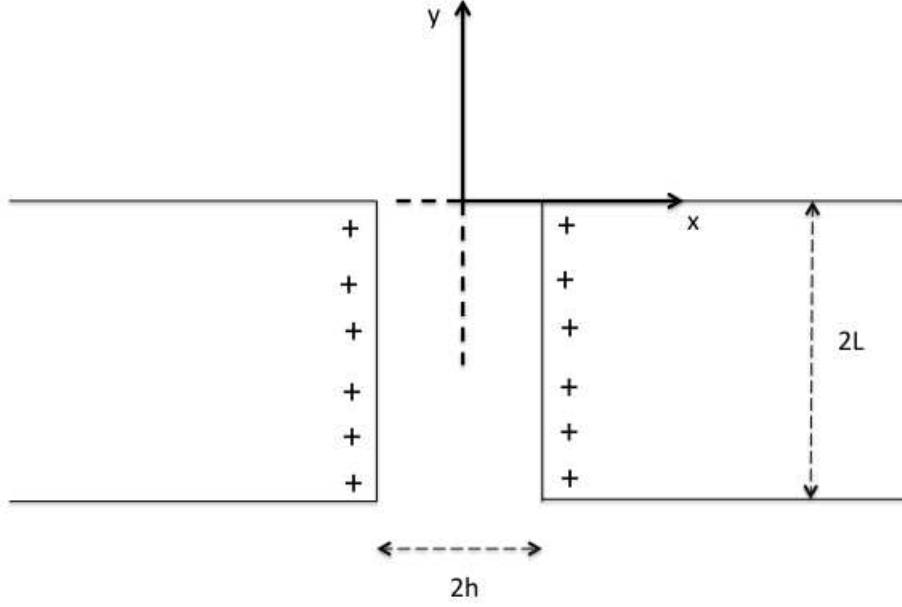


Figure 1: Sketch showing the geometry of the problem and the system of co-ordinates.

interface, on $y = 0$ and $y = -2L$, is uncharged. We assume that the electric potential ϕ is small, with $e\phi/(kT) \ll 1$, where e is the elementary charge and kT the Boltzmann temperature, so that the Debye-Hückel (DH) limit²⁰ is appropriate. We assume that $L, \kappa^{-1} \gg h$, but κL is arbitrary, that is, the length of the channel may be large or small compared to the Debye length. When $\kappa L \rightarrow \infty$ our problem is identical to that considered by Philipse et al.¹⁵ except that we restrict our attention to the low potentials appropriate for the DH approximation. This restriction requires that the surface charge density σ on the surface of the plates should be small, with $\sigma \ll \epsilon \kappa^2 h kT / e$, but leads to simplifications that enable us to investigate the overspill of ions analytically.

We first determine the equilibrium potential $\phi(x, y)$ by solving the DH equation²⁰ $\nabla^2 \phi = \kappa^2 \phi$ in the fluid domain with Neumann boundary conditions: $-\epsilon \partial_n \phi$ equals σ on the opposing faces ($x = \pm h, -2L < y < 0$) but is zero elsewhere on the boundary. Thus, we assume that the ratio of the permittivity of the solid to that of the fluid is sufficiently small that there is no incursion of field lines into the solid. This commonly invoked approximation is reasonable because the dielectric constant of water (~ 80) is much larger than the corresponding values ($\sim 2-4$) for most nonpolar solid substrates. If the channel is infinitely long the potential between the faces is

$\phi = (\sigma/\epsilon\kappa) \cosh(\kappa x)/\sinh(\kappa h) \approx \phi_m \cosh(\kappa x)$, where $\phi_m = \sigma/(\epsilon\kappa^2 h)$. The neutrality length λ defined by Philipse et al.¹⁵ is therefore $\lambda = 2he\phi_m/(kT)$ and the DH approximation corresponds to $\lambda \ll h$.

More generally, when L is finite, we define an average potential $\bar{\phi}(y) = (2h)^{-1} \int_{-h}^{+h} \phi(x, y) dx$ across the channel. Integrating the DH equation across the channel and using the Neumann boundary conditions on the walls, we derive

$$\frac{d^2 \bar{\phi}}{dy^2} = \kappa^2 \bar{\phi} - \frac{\sigma}{\epsilon h}. \quad (1)$$

Since $\kappa^{-1} \gg h$ the equipotential surfaces are almost orthogonal to the channel walls. Thus,

$$\phi(x, y) \sim \bar{\phi}(y) = \frac{\sigma}{\epsilon \kappa^2 h} + A \cosh[\kappa(y + L)], \quad (2)$$

with error $O(\kappa h)^2$.

Next we consider the behavior of ϕ outside the channel at distances $r = \sqrt{x^2 + y^2} \gg h$. In this outer region the potential has cylindrical symmetry and must vanish at infinity. Therefore

$$\phi(x, y) = BK_0(\kappa r), \quad (3)$$

where K_0 is the modified Bessel function of the second kind. In order to determine A and B we desire that ϕ and its derivative match smoothly to the interior potential, Eq. (??), at the channel entrance. This is, however, impossible as $K_0(\kappa r)$ diverges when $r \rightarrow 0$ and the potential Eq. (??) ceases to be valid when $r \lesssim h$. To circumvent this difficulty we consider an intermediate zone consisting of a region of size $\sim h$ outside the pore entrance in order to “bridge” the two potentials.

In the intermediate zone, the potential changes over distances of order h . Thus, $\nabla^2 \phi \sim \phi/h^2 \gg \kappa^2 \phi$, so that the DH equation may be approximated by Laplace’s equation in this region. Specifi-

cally, we need a solution of the Laplace equation consistent with the mixed boundary condition

$$\phi(x, 0) = \frac{\sigma}{\varepsilon \kappa^2 h} + A \cosh(\kappa L) \quad \text{if } |x| \leq h, \quad (4)$$

$$\partial_y \phi(x, 0) = 0 \quad \text{if } |x| > h, \quad (5)$$

and having an electric flux

$$F_e = - \int_{-h}^h \frac{\partial \phi}{\partial y}(x, 0) dx = -2\kappa h A \sinh(\kappa L). \quad (6)$$

We note that since the field vanishes at infinity, the flux F_e is simply related to the charge ΔQ that spills out of the channel at $y = 0$:

$$\Delta Q = -\varepsilon F_e = 2\varepsilon \kappa h A \sinh(\kappa L). \quad (7)$$

A harmonic potential satisfying boundary conditions Eqs. (4)–(7) may be found by considering the solution Φ for potential flow through a slit,²¹ given by

$$\frac{x^2}{h^2 \cosh^2 \Phi} + \frac{y^2}{h^2 \sinh^2 \Phi} = 1. \quad (8)$$

The equipotential lines are ellipses and Φ satisfies the boundary conditions

$$\Phi(x, 0) = 0 \quad \text{if } |x| \leq h, \quad (9)$$

$$\partial_y \Phi(x, 0) = 0 \quad \text{if } |x| > h. \quad (10)$$

To determine the flux, we consider Eq. (8) for $|x| < h$ in the limit $y \rightarrow 0$, for which $\Phi \rightarrow 0$, $\sinh \Phi \approx \Phi$ and $\cosh \Phi \approx 1$. Eq. (8) then reduces to

$$\Phi(x, y) \approx \frac{y}{\sqrt{h^2 - x^2}} \quad (11)$$

in the region $y > 0$ and $|x| < h$. Therefore, the flux is

$$-\int_{-h}^{+h} \frac{\partial \Phi}{\partial y} dx = -\int_{-h}^{+h} \frac{dx}{\sqrt{h^2 - x^2}} = -\pi. \quad (12)$$

The solution satisfying boundary conditions Eqs. (4)–(??) can therefore be expressed as

$$\phi(x, y) = A \cosh(\kappa L) + \frac{\sigma}{\varepsilon \kappa^2 h} + \frac{2}{\pi} \kappa h A \Phi \sinh(\kappa L). \quad (13)$$

We now match the solution in the far field, Eq. (??), to that in the intermediate zone, Eq. (??). The asymptotic properties²² of the Bessel function K_0 for small κr imply that the inner expansion of the outer potential (??) is

$$\phi(x, y) = B K_0(\kappa r) \sim -B \left[\gamma + \ln \left(\frac{\kappa}{2} \right) \right] - B \ln r, \quad (14)$$

where $\gamma \approx 0.577$ is Euler's constant. Next, we consider the asymptotic form of the intermediate solution (??) at large distances from the pore. In this region Φ is large, and $\cosh \Phi \sim \sinh \Phi \sim \exp(\Phi)/2$ so that, by Eq. (??), $\Phi \sim \ln(2r/h)$. Thus the outer expansion of the intermediate solution (??) takes the form

$$\begin{aligned} \phi &\sim \frac{\sigma}{\varepsilon \kappa^2 h} + A \left[\cosh(\kappa L) - \frac{2}{\pi} \kappa h \sinh(\kappa L) \ln \left(\frac{h}{2} \right) \right] \\ &+ \frac{2}{\pi} \kappa h A \sinh(\kappa L) \ln r. \end{aligned} \quad (15)$$

Equating the coefficients in Eqs (??) and (15) we obtain

$$A = -\frac{\kappa \Lambda}{\sinh(\kappa L)} \phi_m, \quad (16)$$

$$B = -\frac{2}{\pi} \kappa h A \sinh(\kappa L), \quad (17)$$

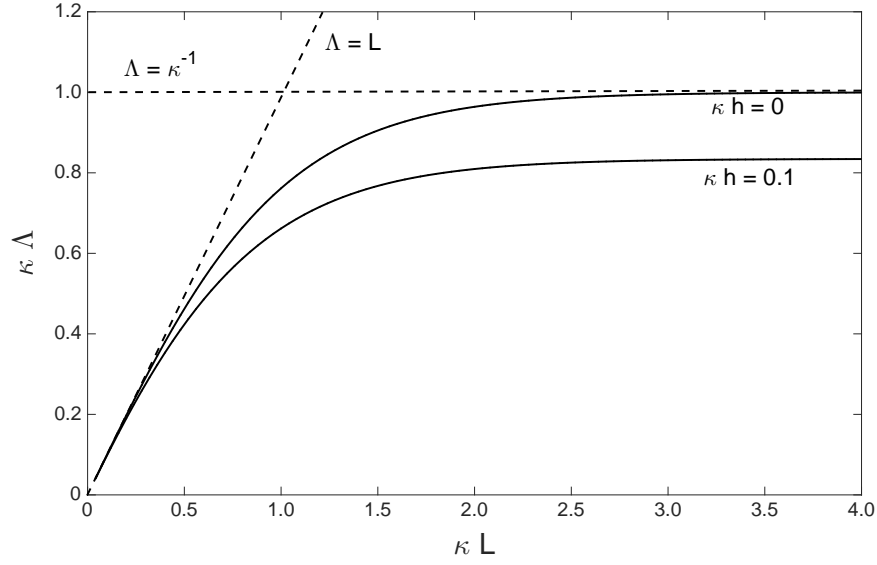


Figure 2: Normalized “lost length” $\kappa\Lambda$ [Eq. (??)] as a function of κL for fixed values of κh .

where the length Λ is defined by

$$(\kappa\Lambda)^{-1} = \coth(\kappa L) + \frac{2}{\pi}\kappa h \left\{ \ln\left(\frac{4}{\kappa h}\right) - \gamma \right\} \quad (18)$$

and $\phi_m = \sigma/(\epsilon\kappa^2 h)$ is the potential between infinite plates.

The length Λ has a simple physical interpretation. Combining Eqs (??) and (16) we see that $\Delta Q = -2\sigma\Lambda$. Thus, the neutralizing charge that would normally be confined within a length Λ of the channel at either end now spills out into the surrounding electrolyte. From Eq. (??) we see that, to leading order in κh , this “lost length” $\Lambda \sim \kappa^{-1} \tanh \kappa L$. Thus, Λ increases from 0 to L as the Debye length κ^{-1} increases from zero to infinity. The dependence of $\kappa\Lambda$ on κL for several fixed values of κh is shown in Figure 2.

We can now construct a composite solution,²³ uniformly valid in $y > 0$, by adding Eqs (??) and (??) and subtracting the solution in the overlap region, Eq. (??). We obtain, after simplification using Eqs (16) and (17),

$$\phi = \frac{2}{\pi}\kappa^2 h \Lambda \phi_m \left[\ln\left(\frac{2r}{h}\right) + K_0(\kappa r) - \Phi \right]. \quad (19)$$

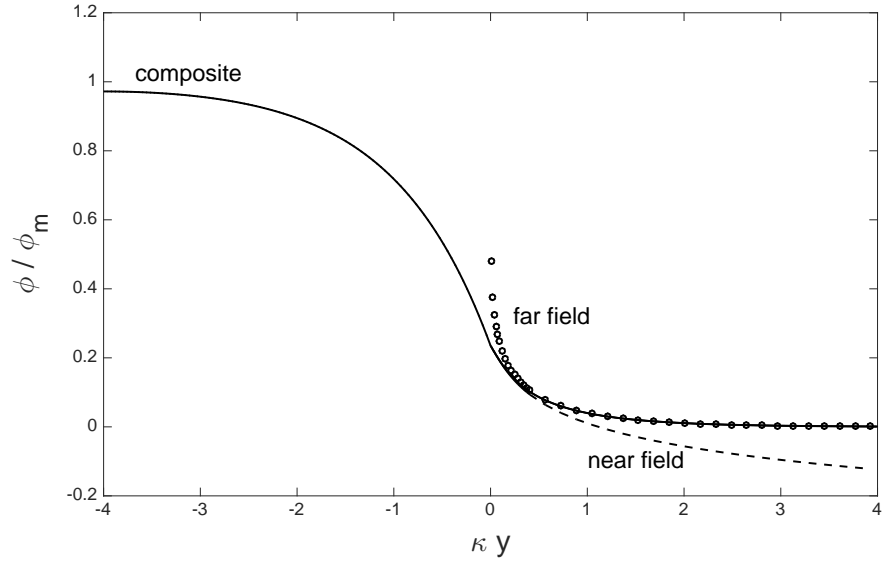


Figure 3: Normalized potential ϕ/ϕ_m on the symmetry axis $x = 0$, plotted against κy . The solid line is the composite solution given by Eq. (??) in $y \leq 0$ and Eq. (??) in $y > 0$. In $y > 0$, the intermediate field Eq. (??) [dashed line] and far field Eq. (??) [symbols], are also shown. Parameter values are $\kappa h = 0.1$ and $\kappa L = 4$ which give [Eq. (??)] $\kappa\Lambda = 0.764$.

An example of the intermediate [Eq. (??)], far field [Eq. (??)] and composite [Eq. (??)] potentials for fixed κh and κL is shown in Figure 3, where the potential $\phi(0, y)$ along the symmetry axis $x = 0$ is plotted. Also shown is the solution in the interior of the channel [Eq. (??)]. Note that there is a discontinuity in $\partial\phi/\partial y$ at $x = y = 0$, though continuity of the mean value of $\partial\phi/\partial y$ across the gap between the plates at the edge $x = 0$ is ensured by Eq. (??). The discontinuity could be eliminated by using the solution of the Laplace equation²⁴ that holds both outside and inside the channel and matches onto both the far-field Eq. (??), and interior Eq. (??) solutions, rather than simply ‘patching’ the intermediate zone to the solution inside the channel. However, the results of such matching differ little from those obtained here that merely ensure continuity of ϕ and of the total flux F_e at $y = 0$.

The repulsive force on either plate is given²⁰ by the integral

$$F = \int_{-L}^{\infty} dy \left[\varepsilon \kappa^2 \phi^2 + \varepsilon \left(\frac{\partial \phi}{\partial y} \right)^2 \right]_{x=0}. \quad (20)$$

It is convenient to express our results in terms of the pressure scale $f_0 = \sigma^2/(2\varepsilon)$. Using Eq. (??), we find the contribution F_1 to the force integral Eq. (??) from the region $-L < y < 0$ within the channel:

$$\frac{F_1}{2L} = \frac{f_0}{\kappa^2 h^2} \left[1 - \frac{2\Lambda}{L} + \frac{\kappa\Lambda^2}{L} \coth(\kappa L) \right]. \quad (21)$$

The contribution from the part of the force integral in Eq. (??) that lies outside the channel consists of the contribution F_2 from the osmotic term that is proportional to ϕ^2 and the electric stress contribution F_3 that is proportional to $(\partial_y \phi)^2$. After integration, these contributions are respectively $F_2 = 8\kappa\Lambda^2 f_0 G(\kappa h)/\pi^2$ and $F_3 = 8\kappa\Lambda^2 f_0 H(\kappa h)/\pi^2$ where the functions $G(x)$ and $H(x)$ are defined as

$$G(x) = \int_0^\infty dt \left[K_0(t) + \ln \left\{ \frac{2t}{t + \sqrt{t^2 + x^2}} \right\} \right]^2, \quad (22)$$

$$H(x) = \int_0^\infty dt \left[\frac{1}{t} - \frac{1}{\sqrt{x^2 + t^2}} - K_1(t) \right]^2. \quad (23)$$

These integrals are well defined, and²⁵ when $x \ll 1$

$$G(x) \sim G(0) = \int_0^\infty K_0^2(t) dt = \frac{\pi^2}{4}, \quad (24)$$

$$H(x) \sim \int_0^\infty \frac{dt}{x^2 + t^2} = \frac{\pi}{2x}. \quad (25)$$

Thus, for small values of κh , we have, $F_2 = 2\kappa\Lambda^2 f_0$ and $F_3 = 4\Lambda^2 f_0/(\pi h)$. The total force is $F = F_1 + F_2 + F_3$ and the disjoining pressure $f = F/(2L)$ is

$$\kappa^2 h^2 \frac{f}{f_0} = 1 - \frac{2\Lambda}{L} + \frac{\kappa\Lambda^2}{L} \left\{ \coth(\kappa L) + \frac{2\kappa h}{\pi} + \kappa^2 h^2 \right\}. \quad (26)$$

If only the leading order in κh is retained, we have the simpler result

$$\frac{f}{f_0} = \frac{1}{\kappa^2 h^2} \left[1 - \frac{\tanh(\kappa L)}{\kappa L} \right]. \quad (27)$$

In the limit $\kappa L \rightarrow 0$, when $h \ll L \ll \kappa^{-1}$, Eq. (??) shows that the average disjoining pressure $f \sim (f_0/3)(L/h)^2$ is independent of the Debye length.

The average disjoining pressure in the limit $\kappa L \rightarrow 0$ can also be derived by considering the free energy of the system. When $L \gg h$, the electric field $E(y)$ is predominantly in the y direction and must satisfy the condition of flux conservation: $2h\epsilon E(y) = 2\sigma y$. Thus $E(y) = \sigma y/(\epsilon h)$, so that the free energy contribution from the region between the plates is $\mathcal{E} = \epsilon h \int_{-L}^L E^2(y) dy = (2\sigma^2 L^3)/(3\epsilon h)$. There is also a contribution to the free energy from the region outside the gap. The electric field $E(r)$ at distances $r \gg h$ satisfies the condition of flux conservation $\pi \epsilon r E(r) = 2L\sigma$ and the free energy contribution from the region outside the gap is $\mathcal{E}' \sim \epsilon \int_h^{\alpha L} E^2(r) \pi r dr = 4\sigma^2 L^2 \ln(\alpha L/h)/(\epsilon \pi)$, where we have replaced the inner and outer limits of integration by h and αL respectively in order to prevent a divergent integral. This artifice accounts for the fact that the electric field is not truly singular as $r \rightarrow 0$ but is determined by the pore geometry in the region $r \sim h$. Moreover, in a real system, the $1/r$ decay of the 2D Coulomb field must give way to a $1/r^2$ decay in 3D, once r exceeds the supposed infinite extension of the slit in the z -direction. This dimension is of course in practice finite and we denote it by αL , α being a large but finite aspect ratio. Therefore, in the limit $h/L \rightarrow 0$, $\mathcal{E}'/\mathcal{E} \sim (h/L) \ln(L/h) \rightarrow 0$. Thus, the force of interaction, F , in the limit $h \ll L$ may be obtained from $2F dh = -d\mathcal{E}$, which gives $F \sim \sigma^2 L^3/(3\epsilon h^2)$ in agreement with Eq. (??) when $\kappa L \ll 1$.

In the opposite extreme of Debye lengths short compared to L (i.e. $h \ll \kappa^{-1} \ll L$) Eq. (??) implies that $F = 2f_0 L/(\kappa h)^2 - 2f_0/(\kappa^3 h^2)$. The first term represents the force in the absence of ion overspill and, as expected, is proportional to L . The second term represents a reduction of force arising from overspill at each of the two edges which results in a drop in the ionic contribution to the osmotic pressure. This quantity is independent of the length L of the plates since field perturbations are confined to distances $\sim \kappa^{-1}$ from the edges. The reduction of the force corresponds to a loss of osmotic pressure within a region of length κ^{-1} at each of the two plate edges. This constitutes an edge correction to the $1/h^2$ scaling law of Philipse et al.,¹⁵ due to the finite size of the plates. Our results for this edge correction can be used for plates of arbitrary shape as long as the radius

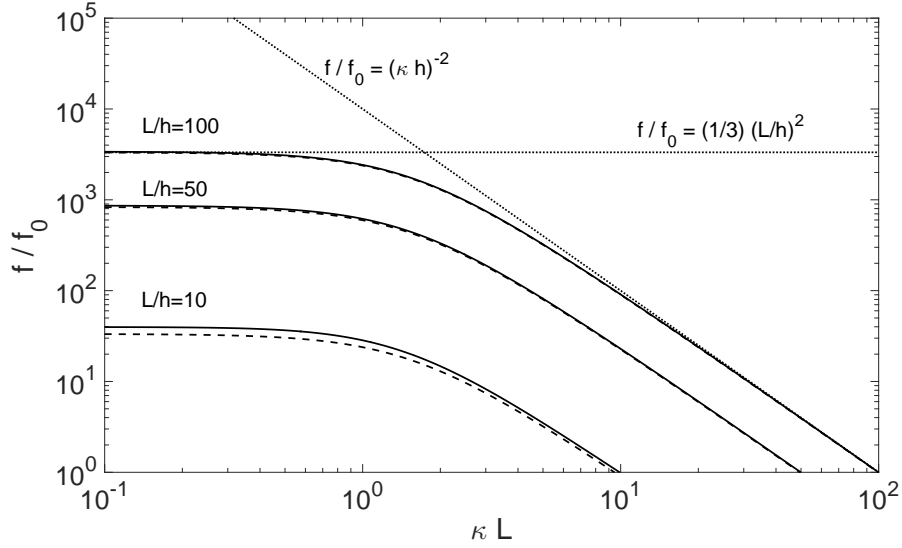


Figure 4: The normalized average disjoining pressure f/f_0 as a function of κL for fixed aspect ratios L/h , evaluated using Eq. (??) [solid lines] and Eq. (??) [dashed lines]. The dotted line of slope -2 corresponds to $f/f_0 = 1/(\kappa h)^2$, the expected result in the absence of edge effects. The horizontal dotted line corresponds to $f/f_0 = (1/3)(L/h)^2$, the limiting value at infinite Debye length. These limits are only shown for the case of $L/h = 100$ for clarity.

of curvature of the plate edges is large compared to the Debye length, so that a locally 2D analysis is appropriate.

Results for f/f_0 as a function of κL , given by Eqs. (??) and (??), are shown in Figure 4, for fixed aspect ratio L/h . This corresponds to a physical experiment in which the interaction force is measured for various electrolyte strengths. We see that at short Debye lengths ($\kappa L \gg 1$), $f/f_0 = 1/\kappa^2 h^2 = (1/\kappa^2 L^2)(L/h)^2$ as reported by Philipse et al.¹⁵ and indicated by the dashed line in the figure. However, as the Debye length becomes large compared to L , the average disjoining pressure does not diverge but approaches the limiting value $(f_0/3)(L/h)^2$, the expected result in the absence of mobile ions.

The reduction in disjoining pressure due to edge effects should be readily observable in interactions between objects of small size, such as nanoparticles. Indeed, in measurements using the scanning force microscope (SFM)¹⁰ the force-distance graph was found to be well described by the Deryaguin approximation when the Debye length was less than 3 nm but not so when the Debye length was increased to 9.6 nm, a value larger than the 7 nm apex radius of the SFM tip. The

discrepancy increases with decreasing plate separation as one would expect from Eq. (??). The geometry in the experimental set up¹⁰ was axisymmetric, rather than plane 2D, making a quantitative comparison with Eq. (??) inappropriate. However, it is clear that the effects discussed in our analysis will also occur in the axisymmetric case.

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References

- (1) Derjaguin, B.; Landau, L. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta Phys. Chim. U.R.S.S.* **1941**, *14*, 633–662.
- (2) Verwey, E.; Overbeek, J. T. G. In *Theory of the stability of lyophobic colloids - the interaction of sol particles having an electric double layer*; Nes, K. V., Ed.; Elsevier: New York, U.S.A., 1948.
- (3) McCartney, L. N.; Levine, S. An improvement on Derjaguin’s expression at small potentials for the double layer interaction energy of two spherical colloidal particles. *Journal of Colloid and Interface Science* **1969**, *30*, 345–354.
- (4) Bell, G. M.; Levine, S.; McCartney, L. N. Approximate methods of determining the double-layer free energy of interaction between two charged colloidal spheres. *Journal of Colloid and Interface Science* **1970**, *33*, 335–359.
- (5) White, L. R. On the Deryaguin approximation for the interaction of macrobodies. *Journal of Colloid and Interface Science* **1983**, *95*, 286–288.

- (6) Bhattacharjee, S.; Elimelech, M. Surface element integration: a novel technique for evaluation of DLVO interaction between a particle and a flat plate. *Journal of Colloid and Interface Science* **1997**, *193*, 273–285.
- (7) Schnitzer, O.; Morozov, M. A generalized Derjaguin approximation for electrical-double-layer interactions at arbitrary separations. *The Journal of Chemical Physics* **2015**, *142*, 244102.
- (8) Israelachvili, J. N.; Adams, G. E. Measurement of forces between two mica surfaces in aqueous electrolyte solutions in the range 0–100 nm. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1978**, *74*, 975–1001.
- (9) Israelachvili, J. Solvation forces and liquid structure, as probed by direct force measurements. *Acc. Chem. Res.* **1987**, *20*, 415–421.
- (10) Todd, B. A.; Eppell, S. J. Probing the limits of the Derjaguin approximation with scanning force microscopy. *Langmuir* **2004**, *20*, 4892–4897.
- (11) Sugimoto, T.; Takahashi, T.; Itoh, H.; Sato, S.-i.; Muramatsu, A. Direct measurement of interparticle forces by the optical trapping technique. *Langmuir* **1997**, *13*, 5528–5530.
- (12) Gutsche, C.; Keyser, U. F.; Kegler, K.; Kremer, F.; Linse, P. Forces between single pairs of charged colloids in aqueous salt solutions. *Physical Review E* **2007**, *76*, 031403.
- (13) Israelachvili, J. N.; Ninham, B. W. Intermolecular forces – the long and short of it. *Journal of Colloid and Interface Science* **1977**, *58*, 14–25.
- (14) Ninham, B. W. On progress in forces since the DLVO theory. *Advances in Colloid and Interface Science* **1999**, *83*, 1–17.
- (15) Philipse, A. P.; Kuipers, B. W. M.; Vrij, A. Algebraic repulsions between charged planes with strongly overlapping electrical double layers. *Langmuir* **2013**, *29*, 2859–2870.

- (16) Olphen, H. V. *An introduction to clay colloid chemistry: for clay technologists, geologists, and soil scientists*; Interscience Publishers, 1963.
- (17) Callaghan, I. C.; Ottewill, R. H. Interparticle forces in montmorillonite gels. *Faraday Discussions of the Chemical Society* **1974**, *57*, 110–118.
- (18) Leote de Carvalho, R. J. F.; Trizac, E.; Hansen, J.-P. Nonlinear Poisson-Boltzmann theory of a Wigner-Seitz model for swollen clays. *Physical Review E* **2000**, *61*, 1634–1647.
- (19) Sherwood, J. D.; Mao, M.; Ghosal, S. Electroosmosis in a finite cylindrical pore: simple models of end effects. *Langmuir* **2014**, *30*, 9261–9272.
- (20) Russel, W.; Saville, D.; Schowalter, W. *Colloidal Dispersions*; Cambridge University Press: Cambridge, UK, 1989.
- (21) Milne-Thomson, L. M. *Theoretical Hydrodynamics*; Dover Publications: New York, U.S.A, 1968.
- (22) Abramowitz, M., Stegun, I., Eds. *Handbook of Mathematical Functions*; Dover Publications Inc.: New York, USA, 1970.
- (23) Hinch, E. *Perturbation Methods*; Cambridge Univ. Press: Cambridge, U.K., 1991.
- (24) Yariv, E.; Sherwood, J. D. Application of Schwarz–Christoffel mapping to the analysis of conduction through a slot. *Proc. R. Soc. A* **2015**, *471*, 20150292.
- (25) Kölbig, K. S. Two infinite integrals of products of modified Bessel functions and powers of logarithms. *Journal of Computational and Applied Mathematics* **1995**, *62*, 41–65.

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